

SF5CF3:

Tuckett, Richard

License:

None: All rights reserved

Document Version

Peer reviewed version

Citation for published version (Harvard):

Tuckett, R 2004, *SF5CF3: the atmospheric properties of this ultimate greenhouse gas*. Government Research Council.

[Link to publication on Research at Birmingham portal](#)

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

SF₅CF₃ : the atmospheric properties of this ultimate greenhouse gas

SRS Annual Review (2004) pp.66-67

Richard Tuckett (University of Birmingham, UK)

Dr R P Tuckett [(T) 0121 414 4425, (E) r.p.tuckett@bham.ac.uk]

Supported by EPSRC, grant number GR/M42794. College areas: Physics, Environmental Chemistry

Abstract: One molecule of SF₅CF₃, an adduct of the SF₅· and CF₃· free radicals, causes more global warming than one molecule of any other greenhouse gas. Using coincidence spectroscopy at the Daresbury SRS, we have determined the strength of the S–C bond to be as large as 3.86 ± 0.45 eV or 372 ± 43 kJ mol⁻¹. This molecule is therefore very unlikely to be removed from the earth's atmosphere by UV photolysis in the stratosphere. Complementary experiments at Birmingham and Super-Aco, Paris have shown that the main sink route of this greenhouse pollutant is low-energy electron attachment in the mesosphere, with Lyman-α photodissociation at 121.6 nm only being a minor channel. By comparison with data for SF₆, the lifetime of SF₅CF₃ in the earth's atmosphere is estimated to be ca. 1000 years.

Text: Serendipity, or being in the right place at the right time, has a long history in science. The accidental discovery of C₆₀ by Harry Kroto et al. in 1985 is perhaps the most famous recent example. In early 2000, by chance I acquired an early preprint of a paper to appear later in the year (Sturges et al., *Science*, (2000) **289**, 611-613). It described the infrared absorption spectrum of a potent greenhouse gas, SF₅CF₃, and its detection in the earth's atmosphere. This molecule is an adduct of the SF₅· and CF₃· free radicals, and its origin is anthropogenic, i.e. man-made. Almost certainly, its source is the reaction of SF₅·, a breakdown product of the dielectric SF₆ in high voltage equipment, with CF₃· on the surface of fluoropolymers ; when the Nuclear Structure Facility was in operation at Daresbury, the local concentration of SF₅CF₃ was probably enormous! Firm measurements made in Antarctica of air samples pumped out of consolidated snow suggested that the concentration of SF₅CF₃ at the end of the 20th century was still very small, ca. 0.12 parts per trillion or 3×10^{11} molecules cm⁻³, but it was growing at the huge rate of 6 % per annum. As important, the strength of the infrared bands suggested that SF₅CF₃ has the strongest radiative forcing, on a per molecule basis, of any pollutant found in the earth's atmosphere. Small problems can become big problems in atmospheric chemistry, and this paper caused an explosion of interest world-wide to study the properties of this unusual molecule, especially those that pertain to its role in the earth's atmosphere. Chemists were particularly interested in the possible sink routes of this molecule from the atmosphere. Could UV photolysis in the stratosphere (15-50 km), the principle cause of ozone depletion by chlorofluorocarbons, remove SF₅CF₃ ? Or was the S–C σ bond strong enough that it survived processes occurring in the stratosphere, and it was removed at greater altitudes by processes in the mesosphere ?

Within months of receiving this preprint, using tunable vacuum-UV radiation in the range 12-25 eV from beamline 3.1 (Seya) of the SRS, we measured the threshold photoelectron – photoion coincidence (TPEPICO) spectrum of SF₅CF₃, and determined indirectly the strength of the S–C bond in the neutral molecule. The apparatus (Fig. 1) incorporates a threshold electron analyser, a linear time-of-flight mass spectrometer, a sodium salicylate window for flux normalisation, and software that allow TPEPICO spectra to be recorded continuously as a function of photon energy. Like CF₄⁺ and SF₆⁺, the ground state of SF₅CF₃⁺ is repulsive in the Franck-Condon region along the S–C coordinate. The onset of ionisation

can therefore only give an upper limit to the energy of the first dissociative ionisation pathway of SF₅CF₃, to CF₃⁺ + SF₅ + e⁻. We have therefore determined the kinetic energy released into the two molecular fragments over a range of photon energies in the Franck-Condon region ; the raw data for CF₄ → CF₃⁺ + F + e⁻ is shown as a 3-d false colour map in Fig. 2. Using an impulsive model for photodissociation, the data for SF₅CF₃ has been analysed and extrapolated to zero kinetic energy. In this way, we determined experimentally the first dissociative ionisation energy for SF₅CF₃ to be 12.9 ± 0.4 eV. Subtracting the adiabatic ionisation energy of the CF₃· radical, 9.04 ± 0.04 eV, we obtained D₀⁰(SF₅-CF₃) of 3.86 ± 0.44 eV or 372 ± 42 kJ mol⁻¹. The atmospheric significance of this value is that the S-C bond is a strong σ bond, and it is highly unlikely that SF₅CF₃ will be broken down by UV photolysis (200-400 nm) in the earth's stratosphere. Subsequently, the electron energy loss spectrum of SF₅CF₃ was measured by Nigel Mason's group, showing that excited electronic states of this molecule, a precursor for photodissociation, do not exist below 8 eV.

We therefore studied the processes that could remove SF₅CF₃ in the mesosphere above *ca.* 60 km ; reactions with small cations, with electrons, and Lyman-α (121.6 nm) photodissociation. The total rate of removal of SF₅CF₃ is then given by

$$\text{Rate} = [\text{SF}_5\text{CF}_3] \cdot \left(\sum_{\text{ions}} k_{\text{ion}}[\text{ion}] + k_e[e^-] + \sigma_{121.6}J_{121.6} \right) \text{ molecules cm}^{-3} \text{ s}^{-1} \quad (1)$$

where k_{ion} and k_e are the bimolecular rate constants for reactions of a cation or electron with SF₅CF₃, $\sigma_{121.6}$ and $J_{121.6}$ are the absorption cross-section of SF₅CF₃ and the mesospheric solar flux at 121.6 nm, and the square brackets signify the concentration of a species. In Birmingham, Chris Mayhew and I measured the rate constants for the reactions of a number of atmospheric cations (*e.g.* N₂⁺, O⁺) with SF₅CF₃ in a selected ion flow tube, and Richard Kennedy measured k_e in an electron swarm apparatus (7.7 × 10⁻⁸ cm³ molecule⁻¹ s⁻¹). At the Super-Aco synchrotron in Paris, I measured the vacuum-UV absorption spectrum between 8 and 20 eV, and determined $\sigma_{121.6}$ to be 1.3 × 10⁻¹⁷ cm². By comparison with analogous data for SF₆, we showed that the ion-molecule term in equ.(1) is insignificant since the ion concentrations in the mesosphere are too low, Lyman-α photodissociation contributes *ca.* 1 %, but the dominant loss mechanism of SF₅CF₃ is low-energy electron attachment to form the dissociative SF₅⁻ anion. The atmospheric lifetime, however, is determined by the slowest step in a multi-step kinetic scheme, which is the rate of transport of SF₅CF₃ from the earth's surface to the mesosphere. The lifetime is estimated to be enormous, *ca.* 1000 years. We are stuck with this potential environmental problem for the foreseeable future!

Chim RYL, Kennedy RA, Tuckett RP, Zhou W, Jarvis GK, Collins DJ and Hatherly PA,
Fragmentation of state-selected SF₅-CF₃⁺ probed by threshold photoelectron – photoion coincidence spectroscopy : the bond dissociation energy of SF₅-CF₃, and its atmospheric implications.
J. Phys. Chem. A., (2001) **105**, 8403-8412

Chim RYL, Kennedy RA and Tuckett RP,
Absorption spectrum of SF₅CF₃ in the range 8-20 eV ; implications for its atmospheric lifetime.
Chem. Phys. Letts., (2003) **367**, 697-703

Kennedy RA and Mayhew CA
Low-energy electron attachment to SF₅CF₃ : atmospheric implications
Int. J. Mass Spectrometry, (2001) **206**, i-iv

Figure 1 Apparatus used to record threshold photoelectron - photoion coincidence (TPEPICO) spectra of SF_5CF_3^+ . Monochromatised vacuum-UV photons in the range 12-25 eV from the Daresbury synchrotron is the tuneable photoionising source of radiation. The apparatus can also record coincidences between either threshold photoelectrons and fluorescence photons (TPEFCO) or photoions and fluorescence photons (PIFCO), but these modes are not used in this study.

Figure 2 TPEPICO-TOF spectra (open circles) for (a) CF_3^+ from CF_4 , (b) SF_5^+ from SF_6 , and (c) CF_3^+ from SF_5CF_3 recorded at photon energies of 16.05, 15.72 and 14.09 eV, respectively. Shown as solid lines, the data fit to mean kinetic energy releases of 0.81, 0.83 and 0.24 eV, respectively.

Figure 3 America is going to be hot in 2154! The images show the results of a computer climate model in which the atmospheric concentration of CO_2 increases at a compound rate of 1% per annum, *i.e.* the concentration doubles in 70 years. The CO_2 concentration then remains constant for 80 years as the climate adjusts to these higher levels. The image on the left shows the predicted temperature rise in the year 2154, that on the right is the 10-year average for the years 2145-2154. In both cases, the temperature changes are relative to a constant concentration of CO_2 at 2004 levels for the next 150 years. Note a big increase in predicted temperature over the populated North America continent, a smaller increase over the less-populated South America continent. The message is clear. We ignore global warming and the effects of pollutants, even minor ones such as SF_5CF_3 , at our peril. Published by permission of Dr Jana Goldman (NOAA) from http://www.gfdl.noaa.gov/products/vis/images/gallery/sphere_04_150.gif

Figure 1

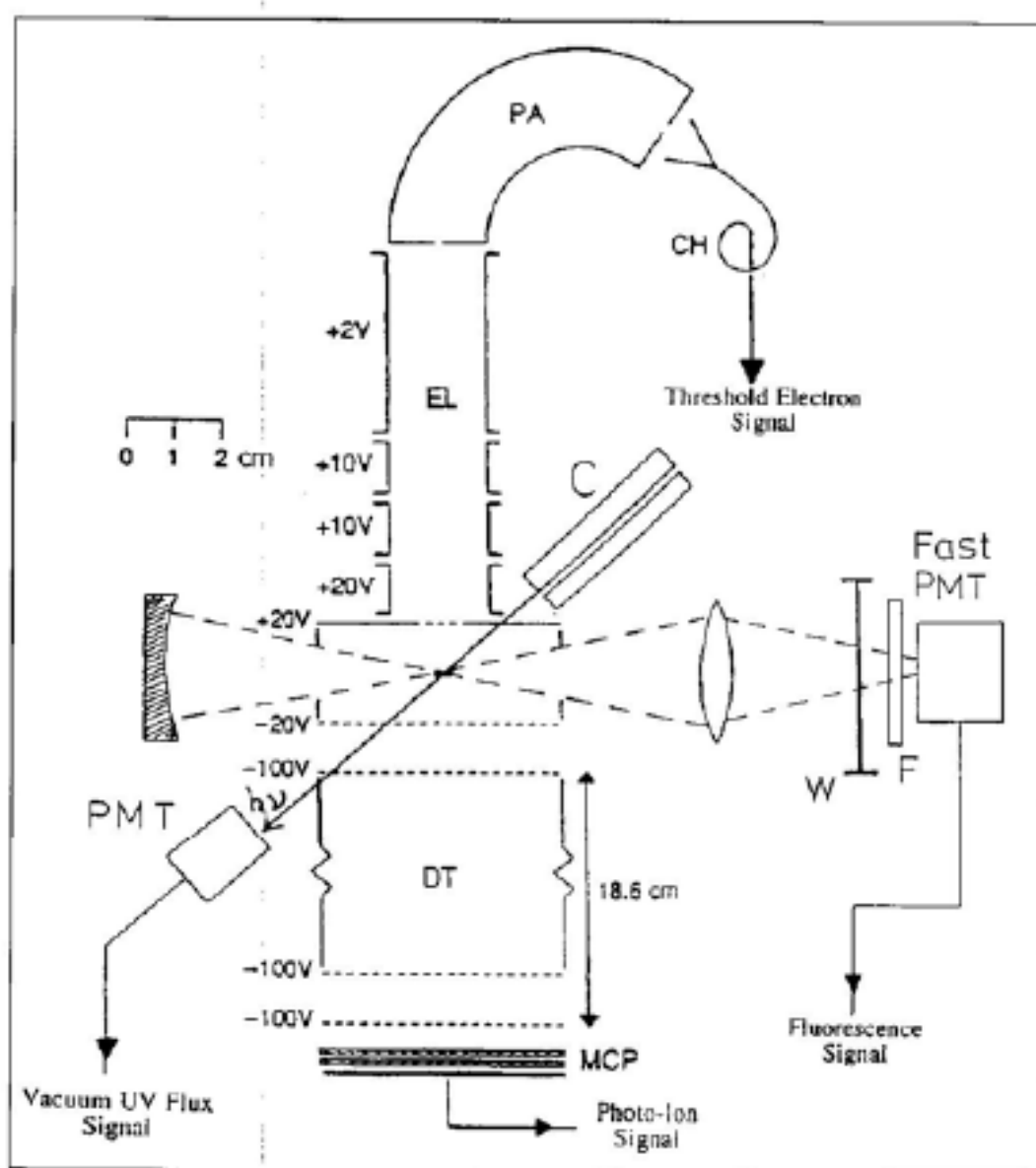


Figure 2

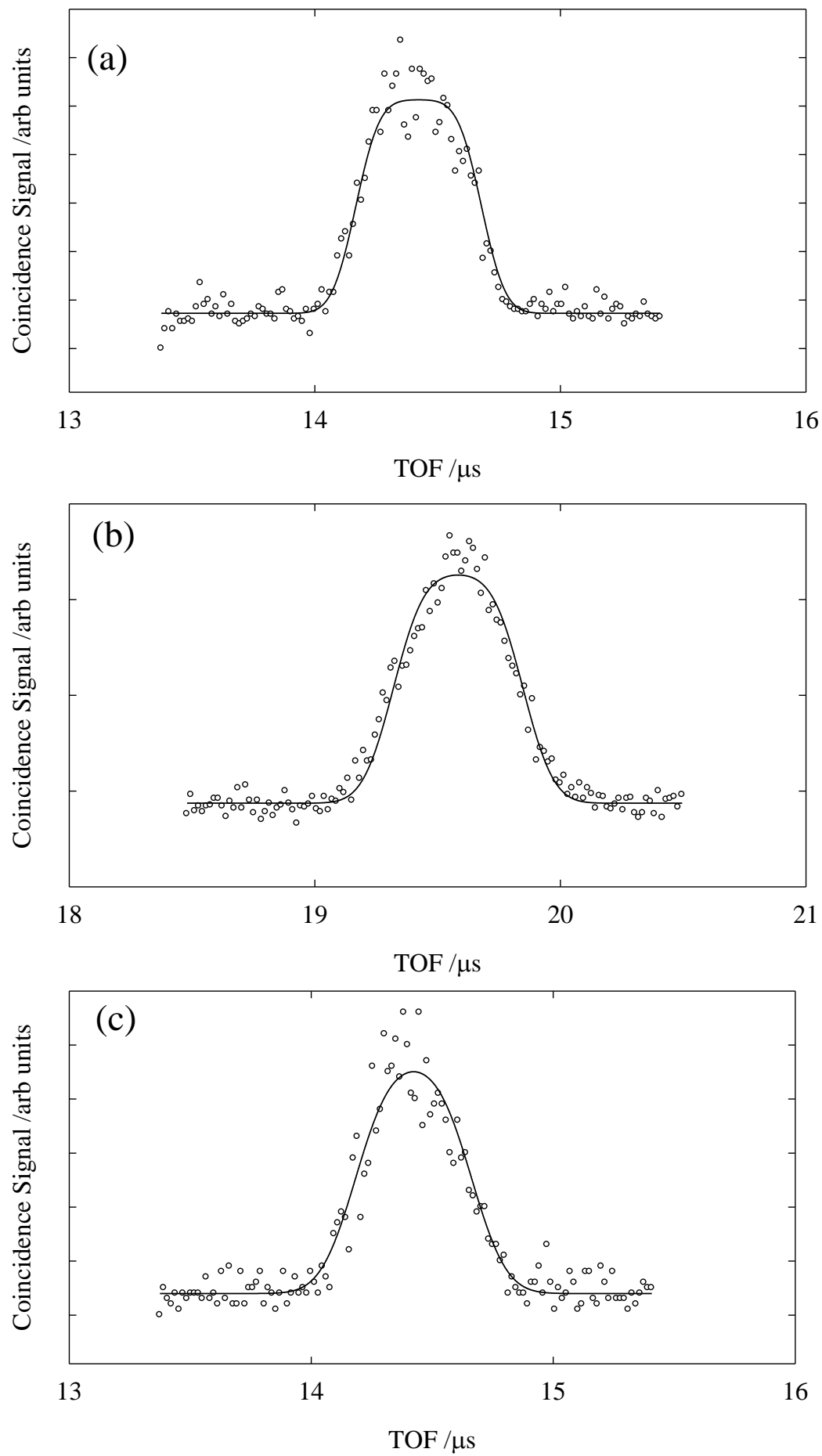


Figure 3

